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## **Abatement of Cu (II), Pb (II) and Zn (II) from highway runoff using agricultural byproduct rice bran**

**Sarita<sup>1</sup>, R. N. Pandey<sup>2</sup>, Upapati<sup>1</sup>, M. K. Mishra<sup>1</sup> and K. K. Singh<sup>1\*</sup>**

<sup>1</sup>*Department of Chemistry, Govt. Post Graduate College, Obra, Sonbhadra(U.P.) India*

<sup>2</sup>*Department of Chemistry, T. D. Post Graduate College, Jaunpur (U.P.) India*

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### **ABSTRACT**

*The rice bran has been used as biosorbent to remove heavy metal ions from highway runoff. It is noted that increase in  $Pb^{2+}$  concentration and pH, caused the increase in adsorption capacity of rice bran. In relation to this, a decrease in rice bran dose results in a higher metal loading on the rice bran. The adsorption isotherms of heavy metals fit the Langmuir and Freundlich model reasonably well. The order of heavy metal adsorption is  $Pb^{2+} > Cu^{2+} > Zn^{2+}$ . A high concentration of co-existing ions such as  $Ca^{2+}$  and  $Mg^{2+}$  depresses the adsorption of heavy metal. Dissolved organic matter (DOM) has a significant influence on metal adsorption. In studies involving column, a long breakthrough time is observed for heavy metals according to the ion selectivity on rice bran. The metal adsorption capacity per rice bran mass in column is lower than that obtained in batch equilibrium tests, which is possibly due to the insufficient residence time and diffusion limitation of the metal. Flushing of the column saturated with heavy metals by 0.1M  $CaCl_2$  solution results in the elution of a highly concentrated metal within shortened pore volumes, implying that rice bran could be re-used for the treatment of heavy metals.*

**Keywords:** Adsorption, Rice bran, Heavy metal, Isotherm, Breakthrough.

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### **INTRODUCTION**

Water ranks second to oxygen and its pollution will perish the world. Highway runoffs have various pollutants such as heavy metals, oil and grease, and particulates from vehicles such as fuels, brake pad wear, and tire wear. In particular, various types of heavy metals are observed in highway runoffs, posing environmental concerns due to their toxic and persistent characteristics.

When there is a storm, the highly polluted runoff from the highway is washed off, directly affecting the water quality near the site [1]. Among them, significant concentrations of copper, lead, and zinc were reported in most literature [2-5].

Many types of structural best management practice (BMP) technologies including porous pavement, catch basins, detention ponds, wetlands, infiltration trenches, complexation, solvent extraction and membrane processes and vegetated swales have been developed for the treatment of runoff containing heavy metals [2,4,6-7]. Meanwhile, adsorption processes have shown many advantages over these physicochemical methods. They are quite selective, effective, and are able to remove very low levels of soluble heavy metals in solution. Therefore, the treatment of highway runoff through a specially constructed filtration/adsorption system can be a promising alternative.

The adsorption of metals has been studied using low-cost sorbents including carbonaceous materials, waste by-products, weathered soils, and natural products such as activated carbon, iron-oxide-coated sand, and zeolites [8-11]. Biological materials are also recently gaining attention as simple, effective, and economical means for the treatment of heavy metals in runoff because they provide effective adsorption capacity and cheaper regeneration cost as compared to conventional sorbents such as activated carbon and ion-exchange resins [7, 9, 12-18]. The adsorption of heavy metals by these biological sorbents is attributed to their constituents which are mainly proteins, carbohydrates, and phenolic compounds containing functional groups such as carboxyl, hydroxyl, and amine groups which are responsible for the binding of metal ions [19]. Conclusively, bio-sorbents would be a feasible option for metal removal in order to develop a suitable highway runoff treatment system. Significantly, rice bran has advantages over other media due to its low cost as well as environmental benefits in terms of reuse of solid waste.

The objective of this study is to investigate the feasibility of utilizing rice bran for the adsorption of heavy metals such as copper, lead, and zinc in solution typically contained in highway runoff. In this work, the adsorption of metals, especially lead on rice bran, was studied using batch kinetic and equilibrium techniques. The equilibrium adsorption data were described by isotherm models. Column tests were also performed to investigate the applicability of the rice bran adsorption system for the treatment of highway runoffs.

## EXPERIMENTAL SECTION

### 2.1. Sorbent and Sorbates

Rice bran was collected from M/s Manoj Rice Mill Industries, Industrial Estate, Chunar, Mirzapur and washed with deionized water for three times to ensure that all fines were removed. The cleaned materials were dried in an oven at temperature of 70°C for 12 hours. The dried materials were then sieved with a #30 mesh (0.6mm) to be used for adsorption tests. The elements C, H, O, and N were determined with an Elemental Analyzer equipped with an inductive furnace analyzer (CE Instruments). The cation exchange capacity of rice bran was measured by a method of NH<sub>4</sub>Ac exchange [20]. Other physico-chemical properties of rice bran were analyzed and are given in Table 1.

The analytical grades of lead nitrate, copper nitrate and zinc nitrate were purchased from Aldrich Chemicals. All heavy metal solutions were prepared in stock solutions of up to 1000 mg/L of metal. Concentrated stock solution was used to make various required dilutions for the adsorption experiments.

**Table 1. Physical and chemical properties of rice bran**

Properties	Value
Particle size (mm)	< 0.6
Water content (%)	4.6 ± 0.10
Volatile matter (%)	48.6 ± 0.12
CEC (meq/100g)	74.3 ± 3.25
Total acidity (meq/g)	0.112
<b>Elemental analysis (%)</b>	
Carbon	47.5
Hydrogen	6.3
Oxygen	41.4
Nitrogen	0.2

## 2.2. Adsorption tests

In the present investigation the batch mode of operation was selected, in order to measure the progress of adsorption. It was carried out by shaking adsorbent (2 gm) with 50 mL aqueous solution of different adsorbate concentrations at different temperatures, pH and contact time. The initial pH of the metal solution was adjusted to the desired value (pH 3.0, 4.5, or 7.0) with 0.1M HCl or 0.1M NaOH. The pH value was measured using a digital pH meter (920A, Orion Inc.). All the bottles were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 125 rpm.. Samples were taken at predetermined sampling times. Five milliliters of the sample was withdrawn at predetermined time intervals, and was filtered using a 0.45 µm syringe filter (PVDF, Millex HV). The filtrates were analyzed by an inductively coupled plasma atomic emission spectroscopy analyzer (ICP-AES, Leeman Abs. Inc.) to measure metal concentration. No correction for volume change was made because the percentage of total volume removed was considered sufficiently small (less than 0.5%).

Adsorption studies were carried out at various initial sorbate concentrations, sorbent doses, and pH values. Additionally, the effects of other ions on the adsorption were evaluated considering the real conditions occurring at the storm water runoff from the highway. Ions of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> concentration varied from 0 M to 0.5 M. Dissolved organic matter (DOM) was obtained by purification of Aldrich humic acid according to the method of Hur and Schlautman [21]. The DOM concentration used in this study was 0, 10, 50, 100 mg/L based on total organic carbon content, respectively. The quantity of adsorbed heavy metal on rice bran was calculated by a mass balance relationship. Duplicate tests were carried out for all experiments, and the mean values were presented.

Column experiments were carried out using a glass column (0.015 m long, 0.025 m i.d.) with an adjustable plunger. The column was packed with 7.2 g of rice bran, and the bed length was kept at 0.03 m. After packing the column, helium gas was used to remove the entrapped air in the sorbent pores. Deionized water was then passed through more than 100 pore volumes to condition the column. The bulk density and porosity were determined gravimetrically as 510 g/L

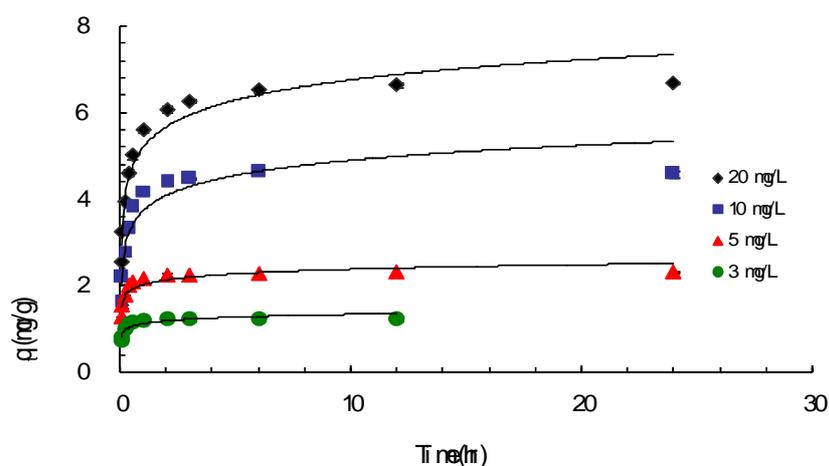
and 0.64, respectively. HPLC pump (Alltech Inc.) was connected to the column, with a three-way valve placed in-line to facilitate switching between solutions with and without heavy metal solution. Conservative tracer tests were carried out using a sodium bromide solution. The tracer solution was regularly taken from the outflow, and its concentration was measured by an ion chromatography (ACME, Younglin Inc.).

The solution of heavy metal mixture (i.e.,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) with an initial concentration of 10 mg/L was pumped through the column at a flow rate of 30 mL/min. The samples were collected at the end of the column at different time intervals, and they were analyzed for metal concentration using ICP-AES. After the adsorption test, flushing of the column with 0.1M  $\text{CaCl}_2$  solution followed, and the samples were collected for analysis.

## RESULTS AND DISCUSSION

### 3.1 Effect of sorbate and sorbent concentration

The adsorption of  $\text{Pb}^{2+}$  as a function of its initial concentration ranging between 3 to 20 mg/L on rice bran is shown in Fig. 1. The adsorption rate was relatively fast at the initial stage, showing that approximately 90% equilibrium was attained within 30 min. This result suggests that the adsorption of  $\text{Pb}^{2+}$  mainly occurred at the surface of the rice bran. After this stage, the adsorption rate became slower, which was probably due to the diffusion of the metal ion into the rice bran. Storm water containing high initial pollutant load is called the first flush, a phenomenon commonly observed at highly impervious sites such as the highway. Initially, high pollutant concentrations in the first flush rapidly decreases after 20-50 min, thereby maintaining relatively low concentrations [22]. Over 90% of metal removal was obtained within the first 30 min of the run, indicating that the rice bran can be an effective adsorption material for the treatment of first flush. The equilibrium time for the adsorption of  $\text{Pb}^{2+}$  on rice bran at different sorbate concentrations was found to be 360 min, which implies that equilibrium time is independent of initial adsorbate concentration.



**Fig. 1.** Adsorption rate of Pb (II) on rice bran (Rice bran dose = 2 g/L, pH = 4.5).

The results given in Table 2 indicate that the adsorption capacities of rice bran increased as  $\text{Pb}^{2+}$  concentration increased. This is possibly due to the gradual increase in electrostatic interactions between rice bran surface sites and increased  $\text{Pb}^{2+}$  molecules [19]. The dosages of rice bran varying from 0.5 to 2 g/L were studied using solutions of 10 mg/L  $\text{Pb}^{2+}$  to evaluate the influence of the sorbent dose on the adsorption capacity. The adsorption capacity of the rice bran decreased as the sorbent dose increased. However, the removal efficiencies of  $\text{Pb}^{2+}$  increased, since the equilibrium concentration of the  $\text{Pb}^{2+}$  in solution was lower in the presence of high concentrations of sorbent. More than 90% of the  $\text{Pb}^{2+}$  could be removed from the solution when the dosage of the sorbent was 2 g/L at the pH of 4.5.

**Table 2. Effect of sorbent dose, initial sorbate concentration, and solution pH on the adsorption of Pb (II) by rice bran**

Sorbent	pH	Sorbent dose (g/L)	Initial Pb(II) concentration (mg/L)	Sorption capacity, $q_e$ (mg/g)	Removal efficiency (%)
Rice bran	4.5	0.5	10	9.28	46.4
		1.0	10	8.32	83.2
		2.0	3	1.48	98.8
			5	2.36	94.6
			10	4.43	88.6
			20	7.84	78.4
	3.0	2.0	10	1.51	30.2
	7.0	2.0	10	4.88	97.6

### 3.2 Effect of pH

The effect of pH on the adsorption of  $\text{Pb}^{2+}$  on rice bran was studied by varying the pH of metal solution from 3.0 to 7.0. The results in Table 2 indicate that the adsorption of  $\text{Pb}^{2+}$  on rice bran was strongly pH dependent, as has been commonly observed for heavy metal adsorption on bio-sorbents [13, 23, 24]. The adsorption of heavy metal on rice bran is attributed to ion exchange with hydrogen ions. Additionally, a number of anionic ligands such as carboxyl and hydroxyl group may take part in the complexation with metal ions at the rice bran surfaces. It was also observed that  $\text{Pb}^{2+}$  removal increased as pH increased. At a low pH, the existence of a relatively large number of hydrogen ions resulted in the depression of the exchange between the metal and the hydrogen ion. Also, the complexes formed via interaction between the metal ions and acidic functional groups were destabilized at a low pH because the stability constants decreased with pH, and therefore, the metal ions eluted into the solution. Also, physical adsorption on the lipophilic part of the rice bran occurred at certain pH ranges where metal was associated with hydroxide and became neutral [25].

### 3.3 Adsorption isotherms

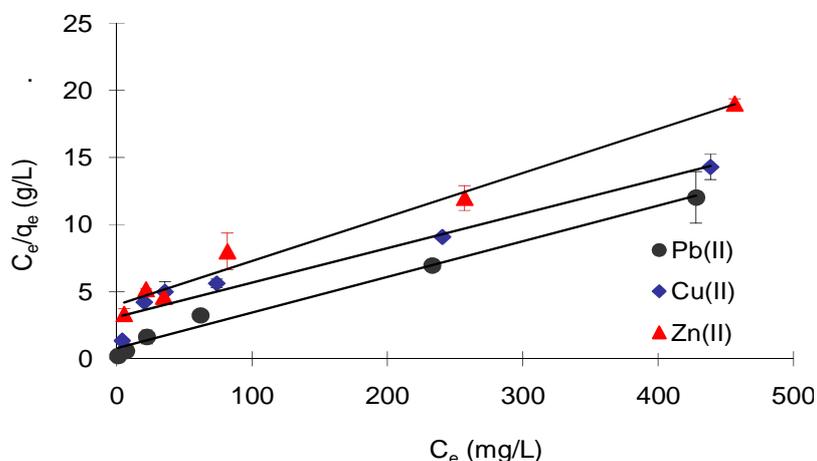
The equilibrium adsorption of heavy metals,  $q_e$  (mg/g), can be related to the equilibrium concentration of these metals,  $C_e$  (mg/L), either by the linear form of the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (1)$$

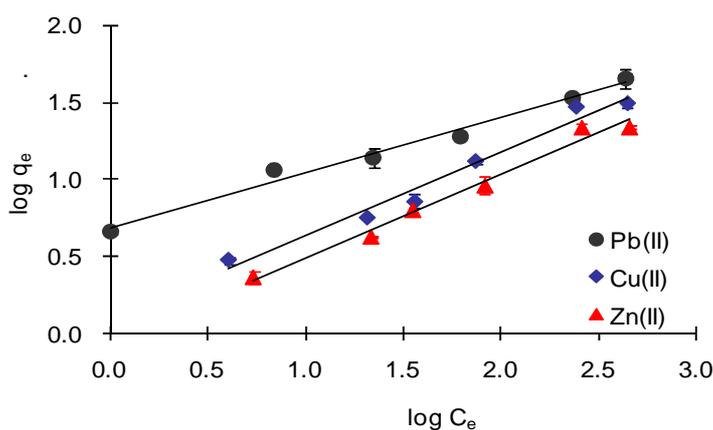
or the Freundlich isotherm model:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where  $S_m$  and  $K_L$  are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.  $K_F$  is the Freundlich constant related to the adsorption capacity, where  $1/n$  is related to the adsorption intensity. The adsorption isotherms of heavy metals were determined for various concentration ranges and fixed mass of rice bran (1g/L of solution). The linear plot of the Langmuir equation was drawn, and the values of  $S_m$  and  $K_L$  were determined by Fig. 2 and also from the slope and intercept of the linear plot of  $\log q_e$  vs.  $\log C_e$  corresponding to  $1/n$  and  $\log K_F$  (Fig. 3).



**Fig. 2.** Langmuir isotherm plot for the adsorption of heavy metals on rice bran (Rice bran dose = 1g/L, pH = 4.5)

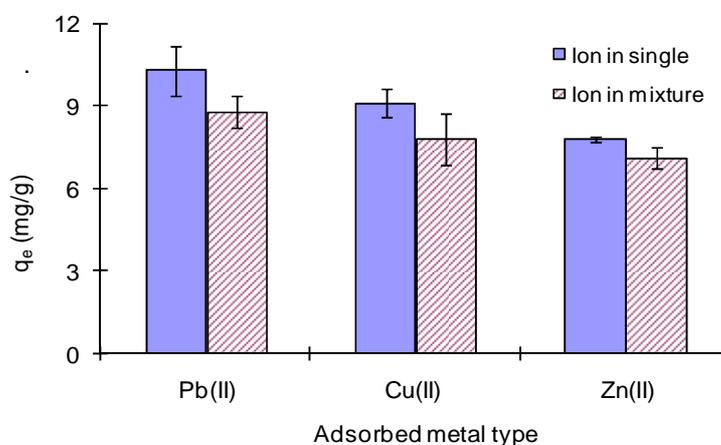


**Fig. 3.** Freundlich isotherm plot for the adsorption of heavy metals on rice bran (Rice bran dose = 1g/L, pH = 4.5)

The equilibrium adsorption of three heavy metals (i.e.,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) were well represented by the Langmuir and the Freundlich model with high  $R^2$  values, as described in Table 3. The suitability of both isotherm models in representing the equilibrium data of three heavy metals indicated that there was the formation of a monolayer of metal ions on the rice bran surface [13]. The order of adsorption affinity on rice bran was  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ , and it was related to the differences in electronegativity of the atom. Considering that the adsorption of heavy metals on rice bran is mainly due to ion-exchanges at the surface level, and found that more electronegative metals show a higher adsorption tendency.

**Table 3. Langmuir and Freundlich adsorption isotherm parameters of heavy metal on rice bran**

Sorbent	System	Metal type	Langmuir constant			Freundlich constant		
			$S_m$	$K_L$	$R_L^2$	$K_F$	$1/n$	$R_F^2$
Rice bran	Metal ion in single	Pb(II)	30.85	0.0132	0.999	2.69	0.385	0.980
		Cu(II)	31.20	0.0071	0.981	1.22	0.505	0.969
		Zn(II)	27.35	0.0068	0.999	1.15	0.510	0.999
	Metal ion in mixture	Pb(II)	35.45	0.0055	0.980	1.05	0.545	0.999
		Cu(II)	29.20	0.0061	0.999	0.86	0.552	0.999
		Zn(II)	29.15	0.0045	0.992	0.45	0.642	0.973

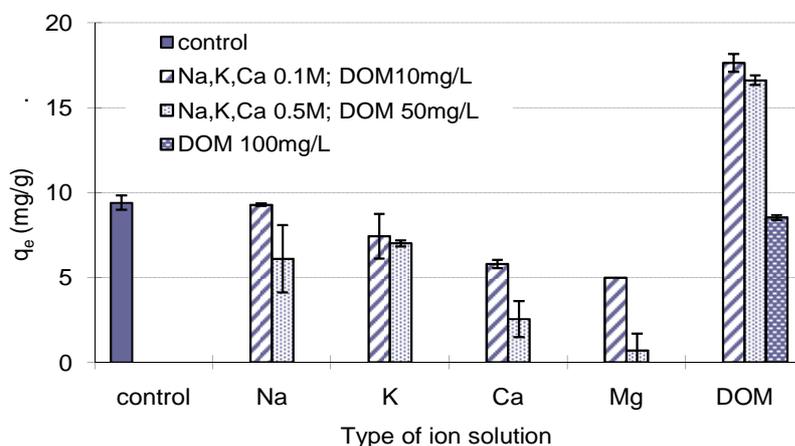


**Fig. 4. Comparison of  $\text{Pb}^{2+}$  adsorption in single and mixture system by rice bran (Initial metal concentration = 100 mg/L, rice bran dose = 2 g/L, pH = 4.5)**

### 3.4 Effects of Co-existing ions

As highway runoff usually contains a mixture of ions and dissolved organic matter [3, 26], the effects of these compounds on the adsorption of heavy metals on rice bran need to be evaluated. In the mixture system of metals, the order of the metal adsorption was  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ , which was consistent to the order of the single metal system (Table 3). It was found that in mixed metal solutions, the adsorption of a particular metal ion on rice bran was less than those if it were present alone, which corresponded to a decrease in removal efficiency (Fig. 4). Also, our results showed that the presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  partially depressed the adsorption of  $\text{Pb}^{2+}$

by rice bran (Fig. 5). In Fig. 5, the control represented the  $\text{Pb}^{2+}$  adsorption in a single system without any other ions. Divalent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  exhibited a stronger inhibition of  $\text{Pb}^{2+}$  adsorption than  $\text{Na}^+$  and  $\text{K}^+$ .



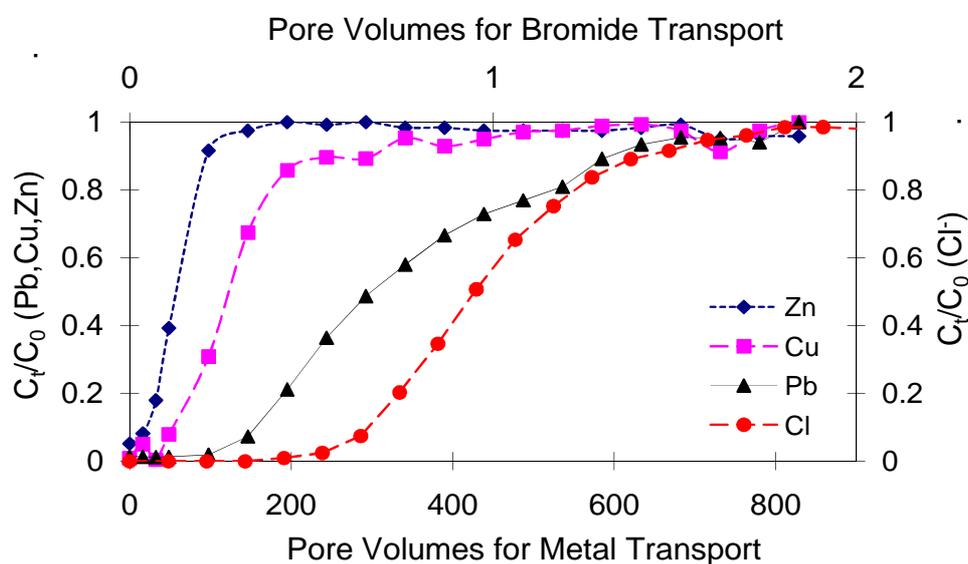
**Fig. 5. Effect of inorganic ions and dissolved organic matter on the  $\text{Pb}^{2+}$  adsorption by rice bran (Initial  $\text{Pb}^{2+}$  concentration = 100 mg/L, rice bran dose = 2 g/L, pH = 4.5)**

This was in agreement with other studies which showed that the inhibition was stronger with higher valent ions than with lower ones [19]. As the concentrations of these ions increased from 0.1M to 0.5M, the effects of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were much more pronounced than those of  $\text{K}^+$  and  $\text{Na}^+$ . Additionally, it was observed that DOM significantly affects the  $\text{Pb}^{2+}$  adsorption on rice bran. At a low concentration of DOM, an enhanced adsorption of  $\text{Pb}^{2+}$  was observed. Generally, DOM strongly affect heavy metal adsorption, since the structure of these compounds contains a large proportion of functional groups such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups [26]. Added DOM was adsorbed on the available surface sites of rice bran, and sorbed DOM reacted with  $\text{Pb}^{2+}$  via complexation, resulting in the increased adsorption of  $\text{Pb}^{2+}$ . As DOM dosage increased, a relative amount of DOM in aqueous phase also began to increase as the surface sites of rice bran became saturated. DOM in aqueous phase then competed with rice bran surface sites and sorbed DOM for  $\text{Pb}^{2+}$  partitioning. Correspondingly, the increased interaction between DOM in aqueous phase and  $\text{Pb}^{2+}$  at a high dose of DOM resulted in the decreased enhancement of  $\text{Pb}^{2+}$  adsorption on solid phase (rice bran).

### 3.5 Column Studies

The results of metal adsorption on rice bran in column were described using breakthrough curves (BTCs) where the concentration ratio ( $C_t/C_0$ ) was plotted versus pore volumes (time). Figure 4 shows that an observed BTC of conservative tracer ( $\text{Br}^-$ ) and a concentration ratio of  $C_t/C_0 = 0.5$  was reached at 1.0 pore volume, implying that the rice bran layer in column was relatively homogeneous. The BTCs of metals showed a large extent of retardation (Fig. 6). The breakthrough curves occurred at about 150, 500, and 800 pore volumes for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ , respectively. As proven from batch tests, the most favorably sorbed metal,  $\text{Pb}^{2+}$ , occupied most of the adsorption sites on the rice bran in column. Therefore, less favorably sorbed metals such as  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  showed more rapid breakthrough. Also, the slope of the  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  curve

was steeper than that of the  $\text{Pb}^{2+}$  curve. This observation implied that the adsorption of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  on rice bran resulted mainly from the ion exchange, while the adsorption of  $\text{Pb}^{2+}$  was not only based on ion exchange, but might likewise involve some physical adsorption [25]. The quantity of  $\text{Pb}^{2+}$  adsorbed in the column was obtained by numerical integration of the area above the BTC. The adsorption capacity per sorbent mass ( $Q_e$ ) was determined to be 1.02 for  $\text{Zn}^{2+}$ , 2.28 for  $\text{Cu}^{2+}$ , and 5.32 mg/g for  $\text{Pb}^{2+}$ , respectively. These values were lower than those obtained from batch equilibrium tests, in which maximum  $Q_e$  was 17.45 for  $\text{Zn}^{2+}$ , 21.15 for  $\text{Cu}^{2+}$ , and 25.62 mg/g for  $\text{Pb}^{2+}$ , respectively. This difference might be due to the intra particular diffusion-limited adsorption rate [16, 17]. Mostly, high flow rate results in the insufficient residence time of the solute and the diffusion limitations of the solute into the pores of the sorbent. It implies that the retention capacity of the adsorption system utilizing rice bran is largely dependent upon the intensity of rainfall by which the flow rate of highway runoff coming into the treatment facility is determined.



**Fig. 6. Breakthrough curves of heavy metals from rice bran-packed column (Metal conc. of feed solution = 10 mg/L).**

The column regeneration was carried out to evaluate the re-utilization of the adsorption system with rice bran. A solution of 0.1M  $\text{CaCl}_2$  was used to elute the heavy metals adsorbed inside the column. The elution curves of the three heavy metals are shown in Figure 7. The curves showed a sharp increase in the beginning followed by a gradual decrease. Also, highly concentrated metal solutions were eluted within shortened pore volumes (time). Opposite the order of the adsorption process, the order of elution of heavy metals was  $\text{Zn} > \text{Cu} > \text{Pb}$ , respectively. The mass of eluted metal was calculated using the elution curve, and it measured 37.8, 10.6, and 6.8 mg for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ , respectively. Most of the heavy metals adsorbed onto the rice bran were eluted, and thus the rice bran could be re-utilized for the repetitive adsorption of metals.

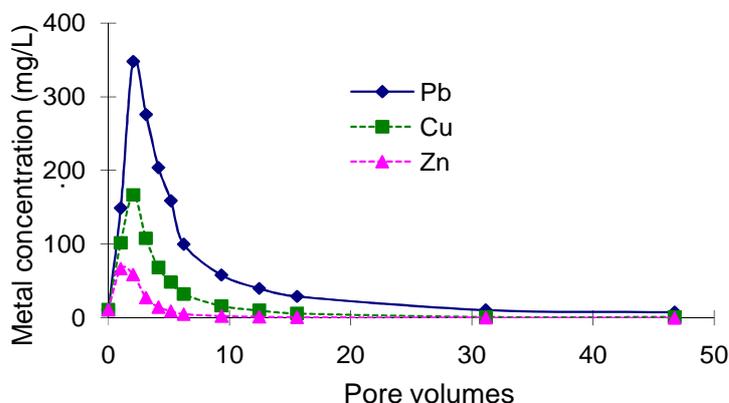


Fig. 7. Breakthrough curves of heavy metals from rice bran-packed column flushed with 0.1M CaCl<sub>2</sub> solution

### CONCLUSION

Rice bran was found to be a cheap and effective bio-sorbent for the removal of heavy metals in highway runoff. Results indicated that the adsorption capacity of rice bran increased along with increases in sorbate concentration and pH. The increase in the rice bran dose resulted in the increased removal rate of heavy metal. The removal of Pb<sup>2+</sup> was rapid at the initial stages, but it became slower afterward. The equilibrium adsorption of heavy metals on rice bran fitted well the Langmuir and Freundlich model. The adsorption capacity of metal varied from one metal system to another, and depended upon the presence of other metal(s) in the solution. Divalent ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>) were more efficient in depressing the metal adsorption on rice bran than monovalent ions (Na<sup>+</sup>, K<sup>+</sup>). DOM showed a significant effect on the metal adsorption on rice bran via the complexation reaction. The enhancement or depression of metal adsorption in the presence of DOM might be largely dependent upon the relative amounts of DOM existing at the aqueous and solid phase (rice bran surface). The results of the column experiments indicate that the rice bran layer exhibited a retarded breakthrough of metals due to high adsorption capacity. The value of adsorption capacity per sorbent mass in column was less than those from equilibrium batch tests. Conclusively, the results of this study suggest that the adsorption system utilizing rice bran is an economically feasible for the treatment of highway runoff.

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